Oak Ridge National Laboratory

3D Printed Hybrid Composite Materials with Sensing Capability for Advanced Vehicles

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June 22, 2022 – 2022 DOE Vehicle Technologies Office Annual Merit Review

Project ID: MAT203

Overview

Timeline

- Start: October 2020
- End: October 2023
- 45% Complete

Budget

- Total Project Funding
- $ 1.5 Million in 3 Years
- $ 500/year in 3 Labs

Barriers

- Continuous fiber (CF) extrusion and 3D printing machine has been demonstrated but needs to be optimized.
- New epoxy and thermoset material blends with the right viscosity and curing behavior for continuous fiber (CF) 3D printing have to be matched. Simulations are needed.
- Fabrication of a sandwiched sensor device and CF composite layers needs to be demonstrated.

Partners

- ORNL: CNMS
- ORNL: CSD
- University of North Texas

Relevance

- Additive manufacturing (AM) enables rapid development of prototype parts and digital manufacturing yet there is an unmet need on high performance parts from continuous fiber composites.
- Materials development and simulation simultaneous with new 3D printing process development is key to improving advanced vehicle manufacturing throughput.
- *If successful,* new vehicle parts development methods can take advantage of AM early with integration of parts design simplification and provision for device health monitoring.

OBJECTIVES

- *1) enhanced organic-inorganic interface for long-term performance via covalent bonding between CF and polymer matrix and,*
- *2) real time evaluation of material properties with embedded sensors.*

… will be addressed in 4 Main Tasks:

Mission statement: *We will pursue research and development of advanced high-performance carbon fiber composites and structures through interfacial chemical optimization in demonstrated additive manufacturing (3D Printing) and structural monitoring through embedded sensors.*

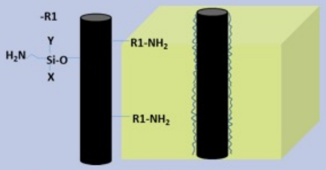
Milestones

	Milestone Description	STATUS	FY	Qtr
1.	**Precise chemical reaction control in composite materials**			
1.1	Study on resin development and chopped carbon fiber composite reactivity	Complete	21	Q1
1.2	Surface modification of low-cost carbon fiber with reactive group	Complete	21	Q4
1.3	Optimized chemical reaction of carbon fiber and polymer matrix	On Schedule	22	Q3
2.	**Computational studies of interfacial failure and mechanical properties**			
2.1	Simulation of Matrix and mechanical properties of a composite*	Complete	21	Q1
2.2	New cohesive models to simulate interfacial interactions continuous CF printing	On Schedule	22	Q2
3.	**3D printing of continuous fiber/composite system with enhanced interface**			
3.1	3D Printing of resin epoxy composite with initial tensile testing measurements	On Schedule	22	Q2
3.2	Optimization of 3D printing process for continuous carbon fiber/polymer composite with ultimate tensile strength > 200 MPa and Young's modulus > 10GPa	On Schedule	22	Q2
4.	**Sensor-embedded fiber/polymer composite with enhanced interface**			
4.1	Sensor material development and compatibilization	Complete	21	Q4
4.2	Combined Composite and 2D materials sensor materials 3D printing	On Schedule	22	Q4

* Paper submitted: "Characterize traction-separation relation and interfacial imperfections by data-driven machine learning models", which was submitted to *Scientific Reports* .

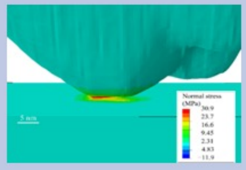
Approach

Precise Chemical Reaction Control



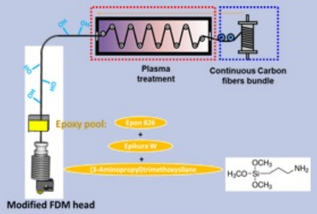
CF/polymer composites with enhanced interface via covalent reactions

Computation Interfacial Interaction



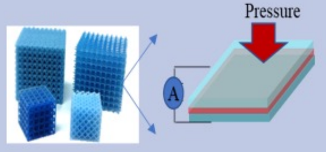
Failure mechanisms of the printed structure & stability by finite element analysis

3D Printing CF /Polymer Composites



Epoxy/continuous CF composites with controlled distribution & adhesion

Embedded Sensor Composite Printing



Embedded mechano-electric sensor synchronously with 3D printed CF composite

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Data for Interface Bonding & Composition

Model for Interface Failure Mechanism & Stability

Novel Printed Structure & IP, Publication

Novel Embedded Sensor & Publication

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The focus is on enhancing interfacial interaction between CF/polymer and monitoring material performance, leading to greater *isotropic* enhanced mechanical properties (Young's modulus >15 GPa and tensile strength> 250 MPa)[1] in technical readiness level (TRL 3) metrics and future TRL 4 studies.

Tasks Summary:

Task 1. Precise chemical reaction control in resin materials

Principal Investigator: Pengfei Cao of ORNL (now with Zoriana Demchuk)

Objective: Develop CF/polymer with enhanced inorganic-organic interface covalent interaction

End-of-project Goal: Composites with optimum chemistry, processability, and high performance.

Collaborators: Rigoberto C Advincula and UNT Group

Task 2. Computational studies of interfacial interaction between polymer matrix and CF

Principal Investigator: Wonbong Choi and Yijie Jiang of UNT

Objective: Simulation of interfacial properties and optimum reactive chemical species

End-of-project Goal: Achieve high correlation of printed components with predictive tools.

Collaborators: Pengfei Cao and Rigoberto Advincula

Task 3: 3D printing of continuous CF/epoxy composite with enhanced fiber-polymer adhesion

Principal Investigator: Rigoberto Advincula of ORNL

Objective: 3D printing continuous CF-epoxy matrix with optimal fabrication parameters.

End-of-project Goal: Achieve AM process and materials combination for high performance.

Collaborators: Pengfei Cao, Yijie Jiang of UNT and Hyrel 3D and TCPoly.

Tasks 4. Continuous sensor-embedded polymer/carbon fiber composite 3D printing

Principal Investigator: Rigoberto Advincula and Wonbong Choi of ORNL and UNT

Objective: 3D print continuous CF/polymers with embedded sensor geometries and testing.

End-of-project Goal: Achieve sensing capability in continuous CF/epoxy 3D printed parts

Collaborators: Pengfei Cao, Yijie Jiang and Hyrel 3D

Accomplishments:

R1

Task 1: Precise chemical reaction control in resin materials

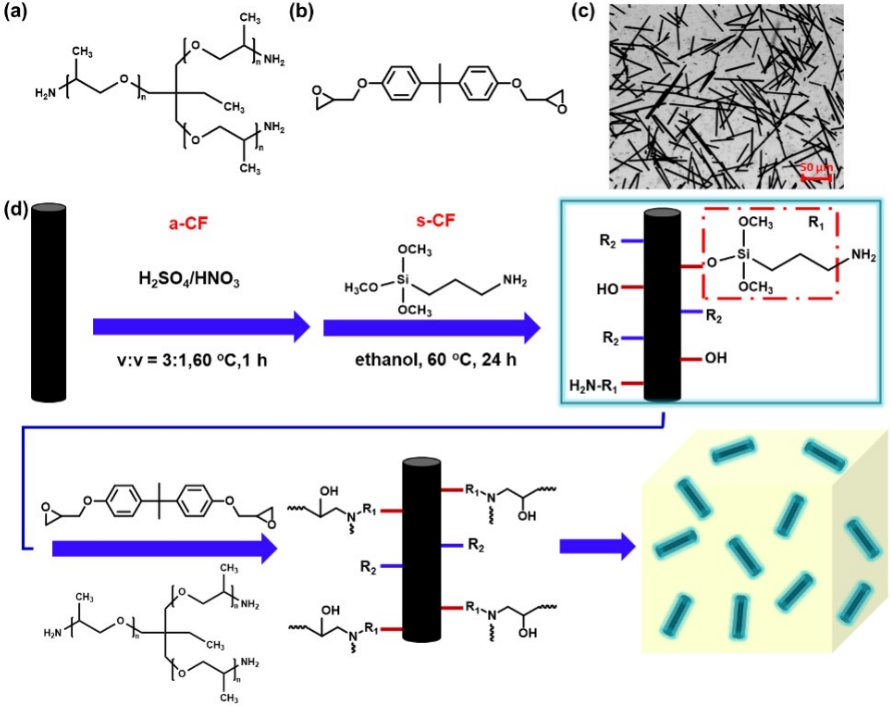
- Various ratios of epoxy precursor and curing agent are mixed at 3:1, 2.5:1, 2:1, and 1.5:1 ratios. High ratios leads to enhanced tensile properties.

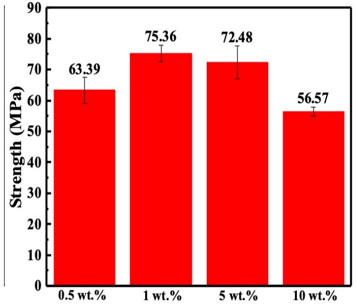
- The mechanical strength of the polymer resin improves when the temperature rises from 80 ^{o}C to 100 ^{o}C, up to 3h.

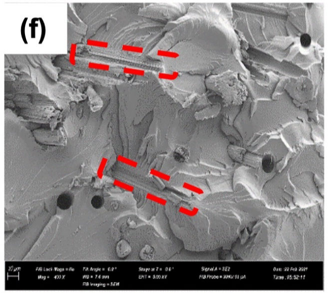
- The amino-functionalized CFs (s-CF) act as additional crosslinkers in the fabrication of epoxy composites, increasing interfacial adhesion via covalent bonding with polymer matrix.

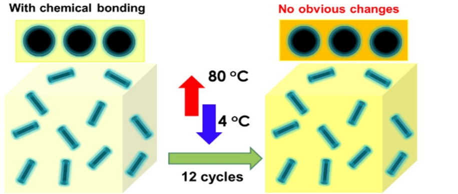
- CF/epoxy composites with CFs (1, 5, 10, 20 wt.%) into the epoxy matrix (3:1 epoxy: amine ratio) at 100 ^{o}C for 3 h.

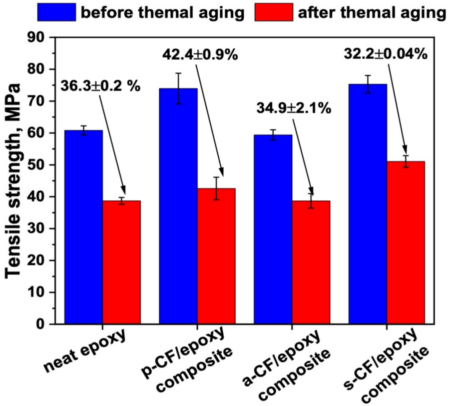
- <u>OPTIMIZED: 3:1 epoxy: amine ratio at 5 wt% CF loaging and cured at 100 ^{o}C for 3 h.</u>

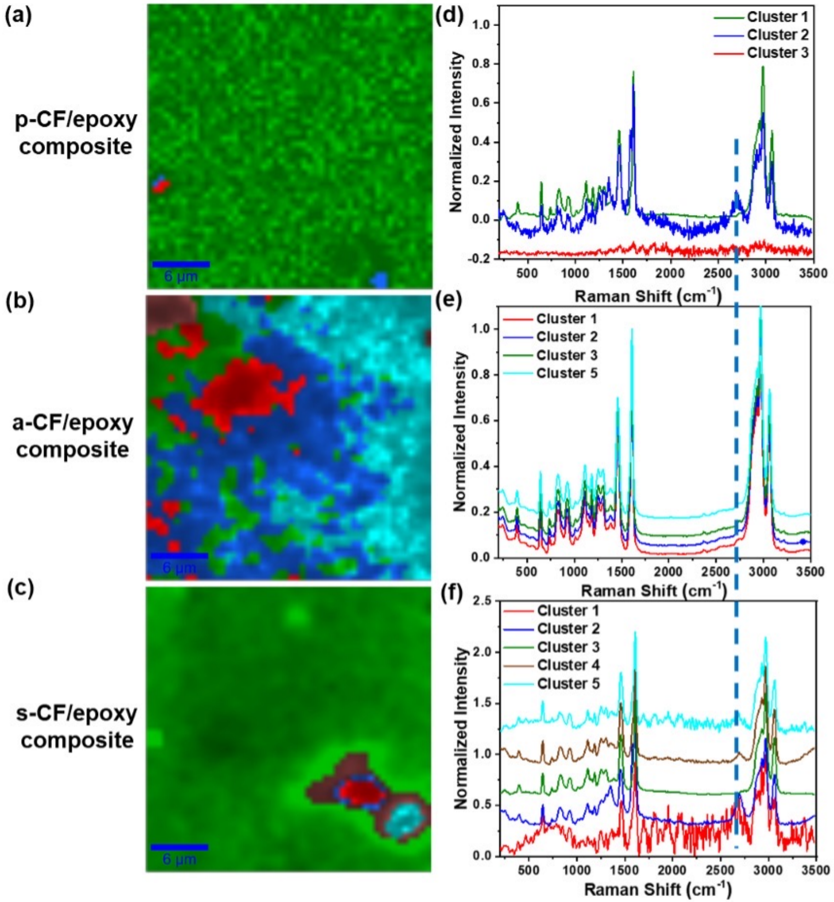










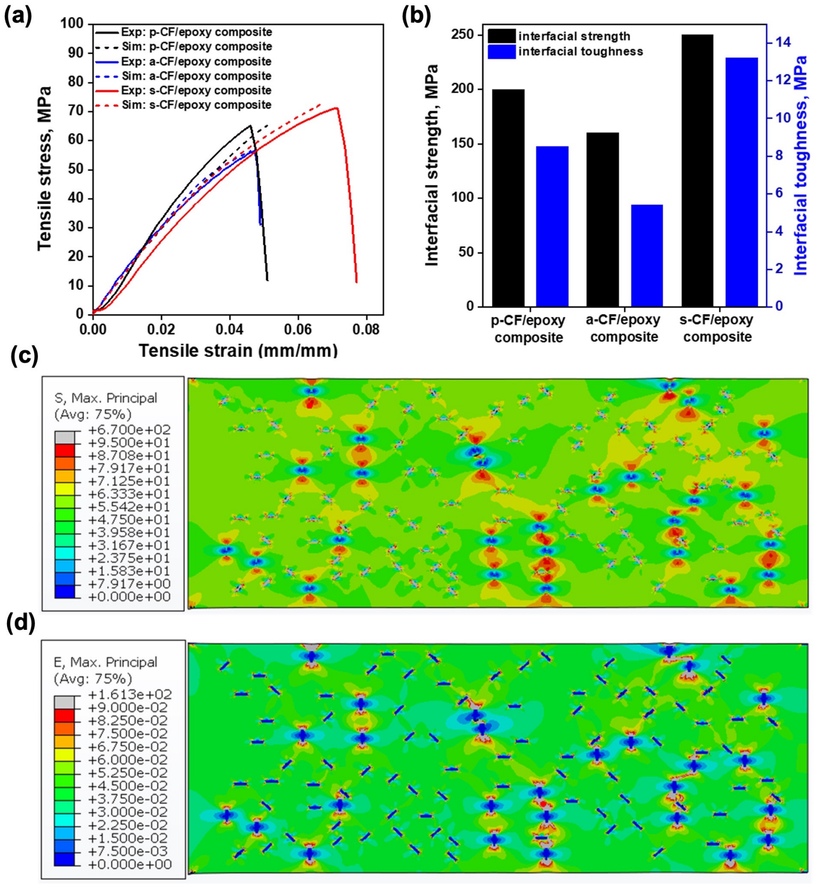


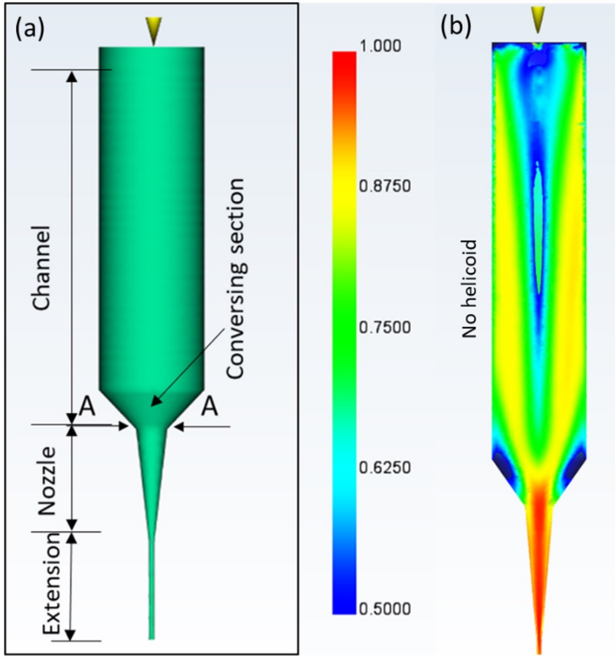
- The effect of CF loading and surface treatment on the ultimate tensile strength: SEM images after tensile test, s-CF/epoxy composite.
- Thermal Cycling: compare the extent of deterioration of tensile strength of the various epoxy composites.
- Raman mapping of (a) the p-CF/epoxy, (b) a-CF/epoxy, and (c) s-CF/epoxy composites confirmed optimization.

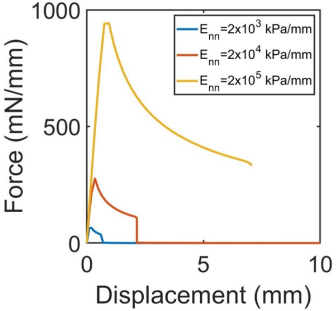
Accomplishments:

Task 2: Computational studies of interfacial interaction between polymer matrix and CF.

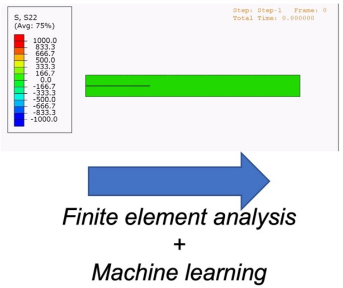
- Optimized data-driven ML models to precisely predict the interface adhesion properties and identify imperfections along interfaces from FEA and standard experiments
- The FEA models are established via a Python-Abaqus customized program, and the interfacial strength and toughness are fitted with experimental data.
- (a) Comparison of stress-strain curves from experimental tests and FEA simulations. (b) The interfacial strength and toughness measurement for 5 wt.% p-CF, a-CF, and s-CF/epoxy composites. (c) The first principal stress and (d) strain contours for s-CF/epoxy composite

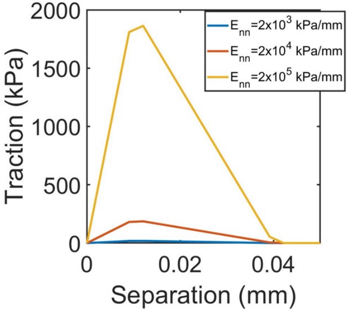




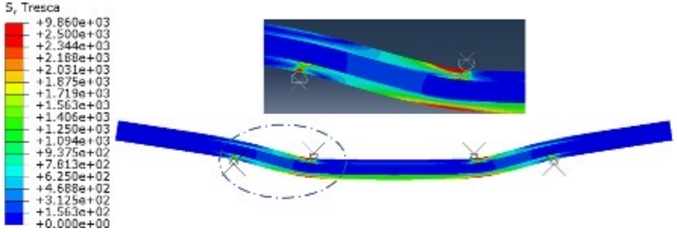


F-D curves:
Macroscale standard double cantilever beam tests





Traction-separation law:
Small scale and intrinsic interfacial property



- Develop a data-driven method based on FEA, machine learning (ML), and simple experiments that characterize interfacial properties without assumptions of predetermined model forms.
- Simulation of extrusion process: non-Newtonian fluid properties, fiber size, grid accuracy.
- Bending tests model: Initial studies using 3 and 4 point bending tests on sandwich CF structures via FEA simulation.

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* Paper submitted: "Characterize traction-separation relation and interfacial imperfections by data-driven machine learning models", which was submitted to *Scientific Reports* .

Accomplishments:

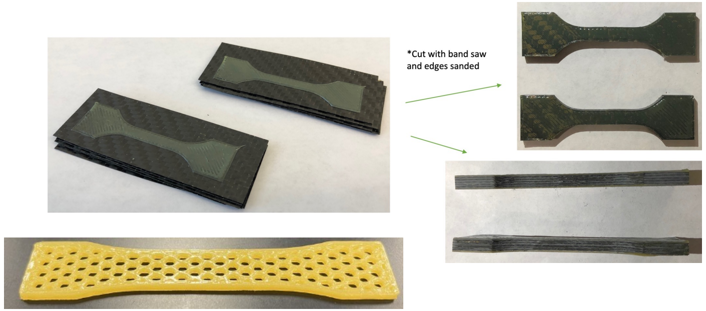
Task 3: 3D printing of continuous CF/epoxy composite with enhanced fiber-polymer adhesion

- 3D Printing of epoxy-milled CF composite was achieved using a viscous solution printing (VSP) based method. The wt% composition was studied from 5 up to 40%

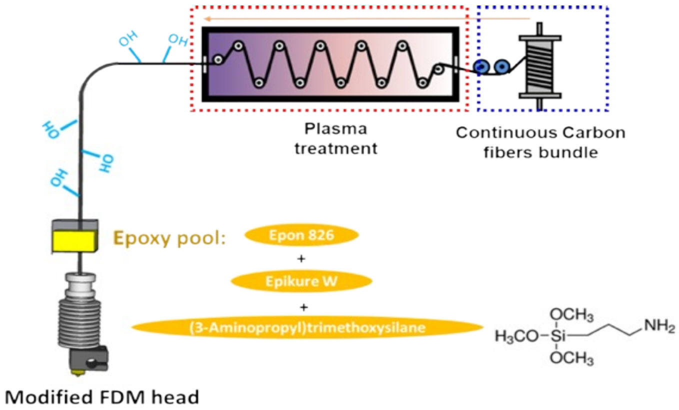
- Rheology and mixing of commercial based epoxy and chopped CF was used to demonstrate upscalability of the process.

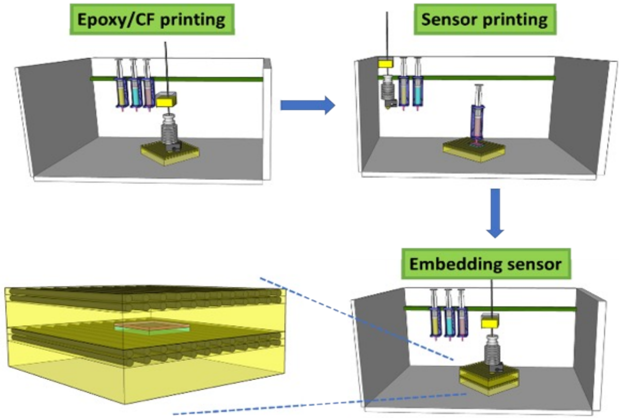
- Sandwich structures using previously CF woven mats and honeycomb patterns being investigated as multilayer structures.

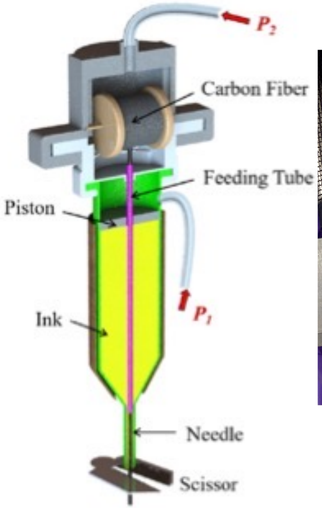
- Continuous CF 3D printing initially achieved but needs further optimization.

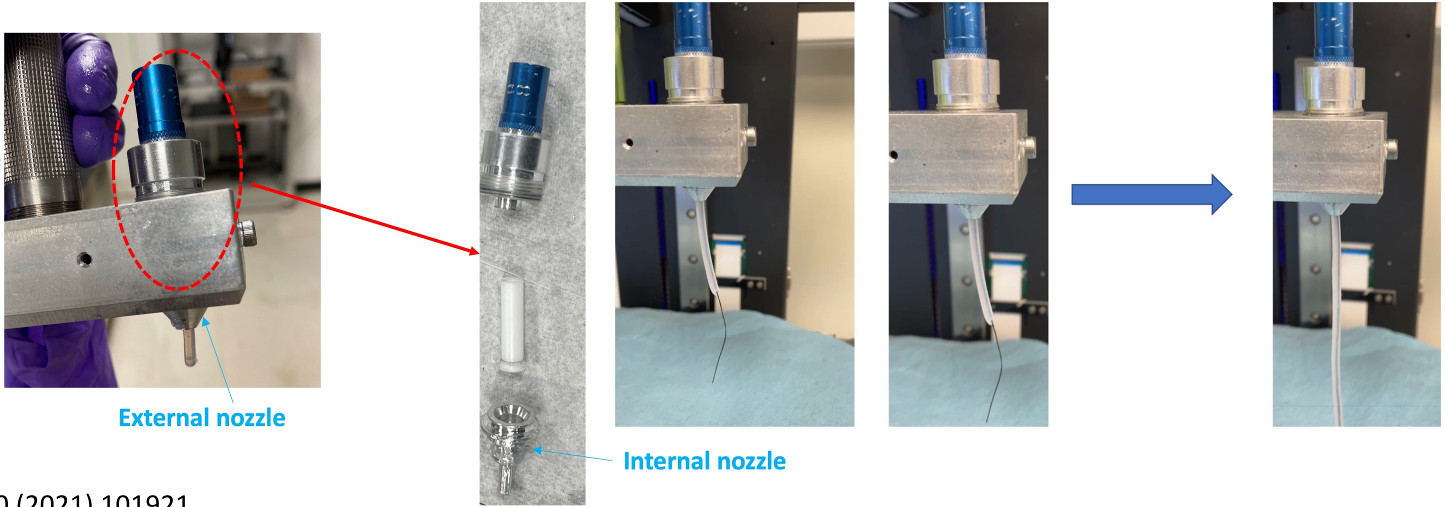


Design for Continuous CF 3D Printing

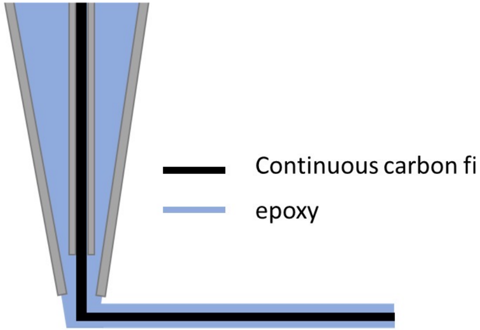


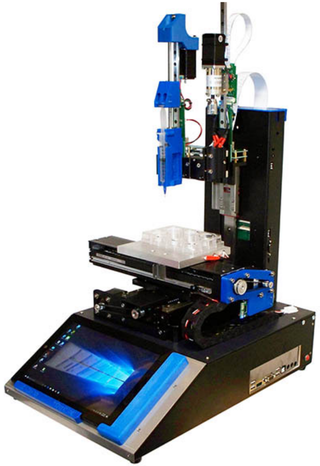






Additive Manufacturing 40 (2021) 101921





- Previous design: Continuous fiber inside a hermitically sealed chamber with back pressure compensation.
- Successful demonstration of continuous fiber-epoxy extrusion using a Hyrel engine and designed attachment.
- *Future work:* Optimization of the rheology of the epoxy matrix with the type of fiber.

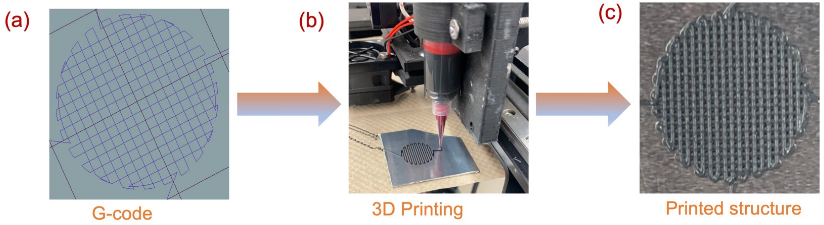
Accomplishments:

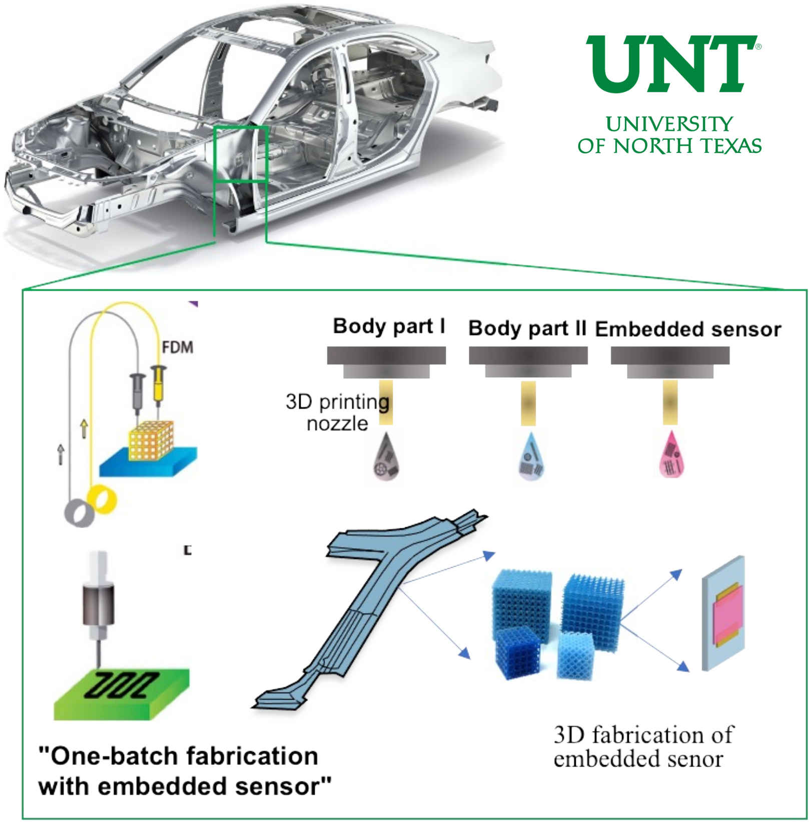
Task 4: Continuous sensor-embedded polymer/carbon fiber composite 3D printing

- The end goal is to design and demonstrate multi-material 3D printing to incorporate in-situ and embedded sensors with the concept of printing vehicle components that can be monitored with stress and time.

- We have developed protocol and 3D printing inks for embedded sensors: V_2O_5 Cathodes: V_2O_5=60 %, PVDF= 25%, CB=15 % and Electrosprayed film of PVDF-MoS_2 Composite: 8% PVDF solution

- Designed and fabricated porous structures of Zn-anode having high surface area for high efficiency Zn-anode with high specific capacity of 650mAh/g.





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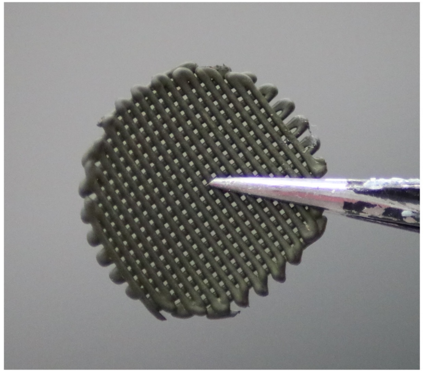

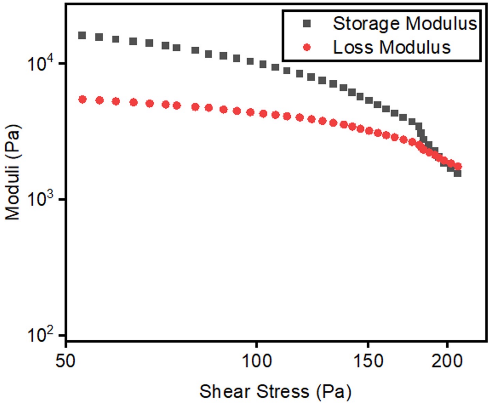

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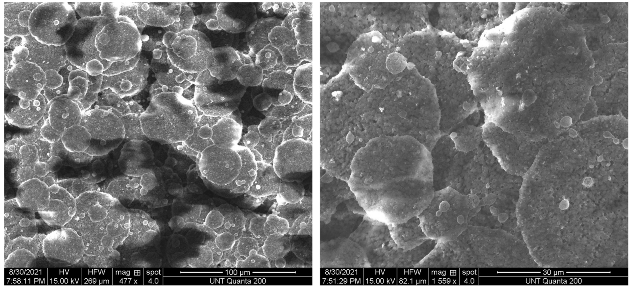
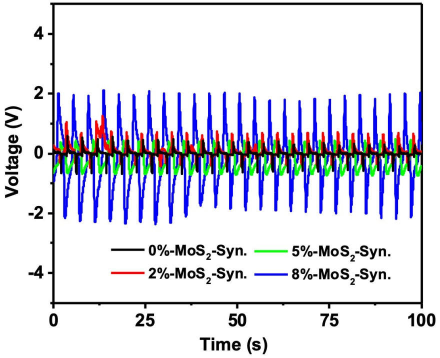
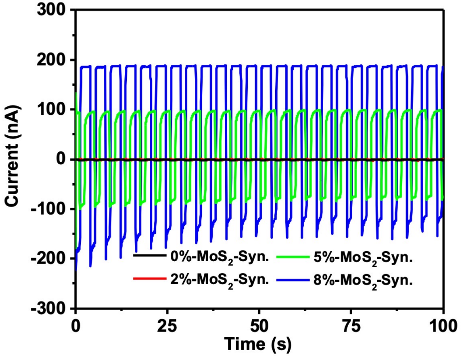
3D Printed Cathodes:
D Printed V_2O_5 Cathode and rheology demonstrating printability of V_2O_5 Ink. Composition: V_2O5=60 %, PVDF= 25%, CB=15 %.

Electrosprayed film of PVDF-MoS_2 Composite:
8% MoS_2 was prepared with PVDF solution. Tuning fabrication parameters to achieve spinning (fibers matrix) or spraying (solid)



SEM of 8% MoS_2 in PVDF. The output voltage and current decreased with adding more than 8% MoS_2. *Next step* is making samples with post-electrical poling and dispersion of MoS_2 with finer MoS_2 particles





Response to Previous Year Reviewers' Comments:

Specifically, the work they have done so far on tasks 1 – 3 to improve the bonding between the epoxy and carbon fiber seems unrelated to "design and fabricate a Zn-anode" in Task 4. Why is it important to improve the bonding of carbon fiber and epoxy?

- In relation to the parallel Zn anode work, Task 4, it is emphasized that our year 3 goal is to eventually have a demonstrated integrated 3D printed part which is also capable of sensing and health monitoring of the structure against early modes of failure. This material will be "sandwiched" between the epoxy printed matrix at the right geometric structure and based on impedance, resistance, or conductance measurement of the final dielectric-electrode material. These measurement are also done early to evaluate their dielectric and transport properties and response as a sensor. *This Task 4 is important to be started in Year 1.*

- *We have since extended the work to V_2O_5 Cathodes and PVDF-MoS_2 Composites as described in this report.*

- Tasks 1-3 as the reviewer noted above are focused on the materials development and 3D printability, i.e. to have a very strong adhesion with the CF surface and the epoxy matrix through surface modification. This includes optimizing the silinization methods, simulating the dispersion and strengthening effects, and then developing 3D printability.

- *This is important as one of the failure modes is that of debonding and delamination due to poor adhesion between the CF filler and the matrix with lack of covalent linkage.* The results in improved tensile properties are described in this report.

Collaboration and Coordination:

- *Since the beginning, the Task leaders and the members of the groups meet continuously every 2 weeks to discuss results and coordinate future work.*

- We have divided the effort into corresponding Tasks in order to have a parallel approach that allow comparison of data and plan for future work more efficiently.

- The coordination between ORNL and UNT is seamless and beyond the regular meeting, a lot of discussions and joint experiments are done in-between group members- email and calls (zoom).

- Successful outcomes on milestones and a first publication has been achieved.

Task 1. Precise chemical reaction control in resin materials: *Pengfei Cao of ORNL*

Task 2. Computational studies of interfacial interaction between polymer matrix and CF: *Wonbong Choi and Yijie Jiang of UNT*

Task 3: 3D printing of continuous CF/epoxy composite with enhanced fiber-polymer adhesion: *Rigoberto Advincula of ORNL*

Tasks 4. Continuous sensor-embedded polymer/carbon fiber composite 3D printing: *Rigoberto Advincula and Wonbong Choi of ORNL and UNT*

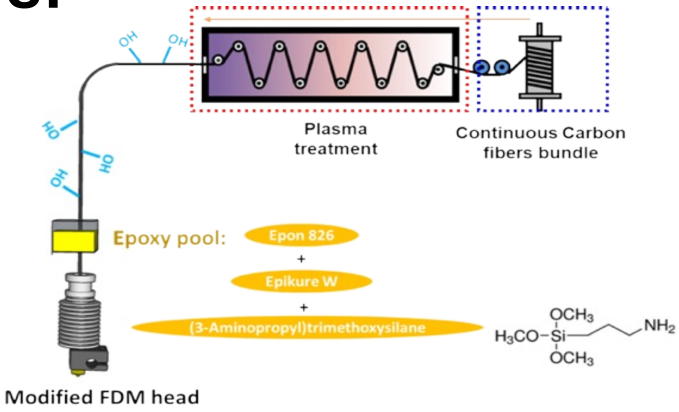
Remaining Challenges and Barriers:

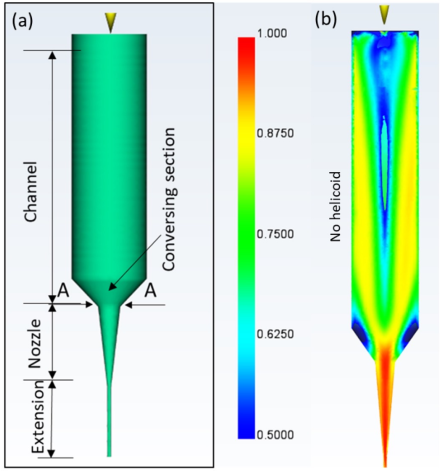
- Continuous fiber extrusion and 3D printing has been demonstrated but optimization of the method is needed - in partnership with Hyrel– Up to 22/Q4

- Optimized epoxy and thermoset materials blends have been achieved but the right viscosity and curing behavior for continuous CF printing has to be met.

- Initial demonstration of a sandwiched sensor device and a fabricated composite layer has yet to be met. The two tasks will eventually be using the same printer platform – Up to 22/Q3.

- Long-Term: demonstrated AM (3D Printing) and structural monitoring through embedded sensors. Simulation studies is essential for robust materials and process design.





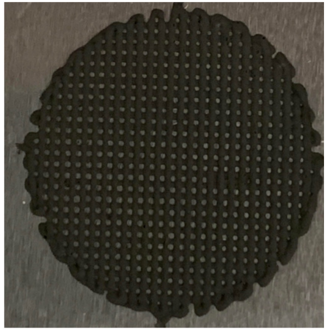
Proposed Future Research: FY 2022-2023

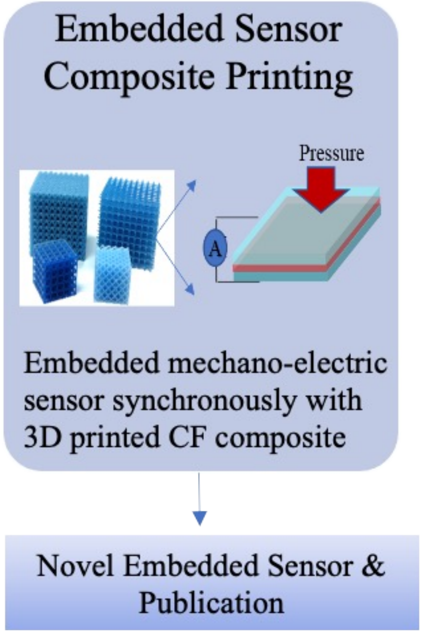
- Demonstrate *optimized* continuous CF – epoxy 3D printing into larger structures with optimized formulations.

- Investigate long-term thermo-mechanical properties of CF/polymer composites tandem with simulations using FEA and genetic algorithms for optimized 3D printing methods..

- Investigate other modes of surface modification of CF including use of other sizing and surface modifiers (silanes, phosphonates, crown ethers, etc.) with various wt% CF/epoxy composites in a continuous carbon fiber/epoxy 3D printing system.

- Sandwiching of 3D printed sensor (Zn, Va, Mo, etc. and develop a high-resolution sensor with the epoxy/CF composite.





Any proposed future work is subject to change based on funding level

Summary

OPERATIONAL HIGHLIGHTS

- Four Tasks on schedule with short-term (FY-22) and path for long-term (FY23)
- Cohesive team between ORNL and UNT that meets regularly: every two weeks.
- Submitted and Published several papers already.

TECHNICAL ACCOMPLISHMENTS:

- A comprehensive study of epoxy/chopped CFs has been accomplished; Optimized epoxy resins with optimized protocols for grafting of surface functional groups in CFs.
- Established data-driven ML models to precisely predict the interface adhesion properties and identifed imperfections from FEA and developed algorithms for material programming.
- 3D Printing of epoxy-CF composite was achieved using a viscous solution printing (VSP) based method including continuous CF 3D printing.
- Developed a protocol and 3D printing inks for embedded sensors and fabrication with epoxy/CF composite.

PUBLICATIONS

Integrating helicoid channels for passive control of fiber alignment in direct-write 3D printing, Additive Manufacturing, Volume 48, Part B, 2021, 102419, https://doi.org/10.1016/j.addma.2021.102419.

Characterize traction–separation relation and interfacial imperfections by data-driven machine learning models. *Sci Rep* **11,** 14330 (2021). https://doi.org/10.1038/s41598-021-93852-y